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BUBBLE-POINT PRESSURES AND LIQUID DENSITIES OF R-32, R-125 AND R-143a MIXTURES

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ABSTRACT

In the present paper, the measurements of the bubble-point pressures and the liquid densities of refrigerant mixtures composed of R-32, R-125 and/or R-143a are reported for temperatures from 280 to 320 K in 10 K intervals and for entire compositions. An experimental apparatus used is a magnetic densimeter coupled with a variable volume cell. Based on the measured bubble-point pressures, the optimization of the binary interaction parameter of the Peng-Robinson equation, which reproduces the available data within $\pm 1\%$ in pressure, has been discussed. Empirical correlations to represent the saturated-liquid and compressed-liquid densities within $\pm 0.4\%$ have also been developed.

INTRODUCTION

Under the accelerating international regulations on HCFC refrigerants, R-502 and R-22 are still dominantly being used for low temperature commercial refrigeration systems. It is therefore urgent to consider the potential substitutes to replace these conventional refrigerants. Binary and/or ternary mixtures composed of R-32, R-125 and/or R-143a are expected as the potential alternatives to R-502 and R-22 due to their near-azeotropic properties so that they would behave similarly with pure compounds. In accord with an increasing concern about these mixtures, the present study aims systematic measurements of the bubble-point pressures and the liquid densities for a wide range of compositions and temperatures since only a limited number of data is available up to the present.

Based on the measured bubble-point pressures we have optimized the binary interaction parameter of the Peng-Robinson equation. We have also developed empirical correlations to represent the saturated-liquid and compressed-liquid densities. A comprehensive comparison with available data is also discussed.

EXPERIMENTAL

A magnetic densimeter coupled with a variable volume cell has been used to measure the liquid phase PVT_x properties of the binary and/or ternary mixture of R-32, R-125 and R-143a. The experimental apparatus shown in Fig. 1 consists of a temperature-control and measuring subsystem, a pressure-control and measuring subsystem, and a density measuring subsystem. The temperature is determined by means of a platinum resistance thermometer placed in the vicinity of the magnetic densimeter immersed in a thermostated fluid bath. The pressure is measured through a quartz-pressure transducer, while the density is obtained by using the magnetic densimeter. By combining the magnetic densimeter with the variable volume cell equipped with the metallic bellows, it becomes possible to achieve a vapor-liquid coexisting two-phase state or a compressed-liquid phase of the sample liquid. The bubble-point is determined by careful visual observation of the appearance and reappearance of a minute bubble in the liquid phase. In case of mixtures, the mixture composition is determined by weighing the mass of supplying vessels before and after the sample filling with an aid of its condensation into the variable volume cell. Some more detailed description with respect to the present

experimental apparatus and procedures have been reported in our earlier publications[1-3] which reported similar measurements with respect to the binary R-32/125 and R-125/143a systems. Namely, the present study was performed so as to achieve a complete coverage of the binary and ternary systems consisted of R-32, R-125 and R-143a incorporated with our earlier measurements [1-3].

The present study covers the binary R-32/143a and ternary R-32/125/143a systems for temperatures from 280 to 320 K and for entire compositions. The estimated experimental uncertainties of the present measurements are not greater than ± 8 mK in temperature, ± 10 kPa in pressure, $\pm 0.2\%$ in density and ± 0.3 mass% in composition, respectively.

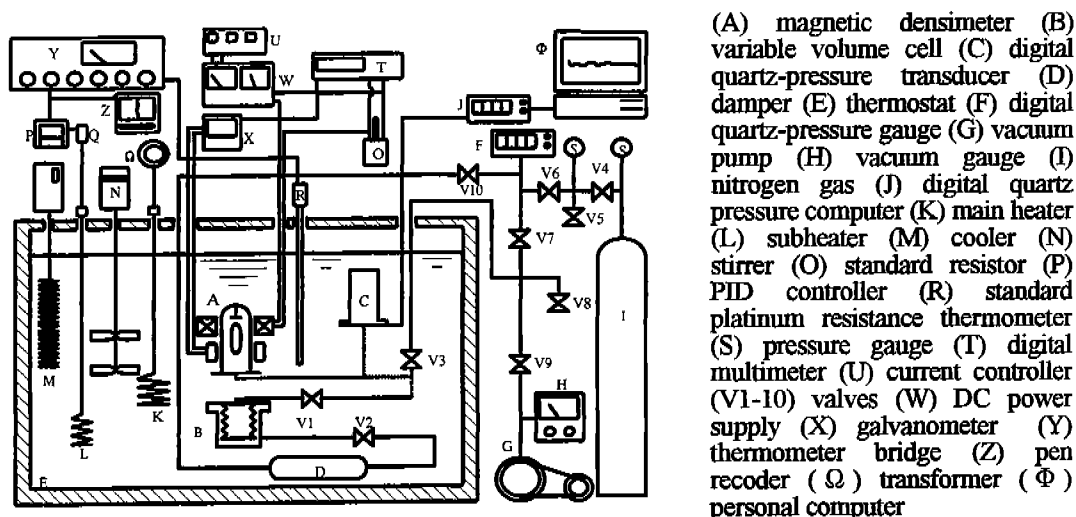


Fig. 1 Experimental apparatus

RESULTS AND DISCUSSION

Figure 2 shows a typical example of the measured bubble-point pressures of refrigerant mixtures of the present interest at 300 K. The bubble-point pressures at other temperatures in the present study show similar behavior as that illustrated in Fig. 2. As reported elsewhere [1], the binary R-32/125 system is an azeotropic mixture with a minimum temperature existing in the vicinity of composition of 80 mass% R-32. The binary R-125/143a system is also considered an azeotropic blend with a maximum temperature especially at lower temperature. Concerning the ternary R-32/125/143a system, any azeotropy has not yet been confirmed due to limited data for a single composition in the present study. However, based on our calculation of the bubble-point and dew-point pressures for the ternary R-32/125/143a system, it seems that the ternary R-32/125/143a system is a zeotropic blend.

Table 1 Parameters optimized for the PR equation

Properties	R-32	R-125	R-143a
T_c / K	351.26 ^a	339.17 ^a	345.88 ^a
P_c / MPa	5.780 ^a	3.620 ^a	3.764 ^a
$\rho_c / \text{kg} \cdot \text{m}^{-3}$	427 ^a	577 ^a	431 ^a
$M / \text{g} \cdot \text{mol}^{-1}$	52.024	120.02	84.04
ω^*	0.277 ^b	0.306 ^b	0.263 ^b

^a Higashi [4], ^b Yoshida et al. [5]

*acentric factor

All the lines in Fig. 2 are the isopleths calculated from the Peng-Robinson (PR) equation [6] whose parameters are summarized in Table 1. The binary interaction parameter used for calculating the bubble-point pressures of the binary R-32/143a and R-125/143a systems are optimized as constant, while that of the binary R-32/125 system is given as a function of temperature. The optimized binary interaction parameters, k_{ij} , are given in Table 2 where T denotes temperature in K.

Table 2 Binary interaction parameters for the present binary systems

Binary system	k_{ij}	Effective range
R-32/125	$-0.0466+0.000169T$	280 – 320 K
R-32/143a	0.0116	280 – 320 K
R-125/143a	-0.0126	200 – 330 K

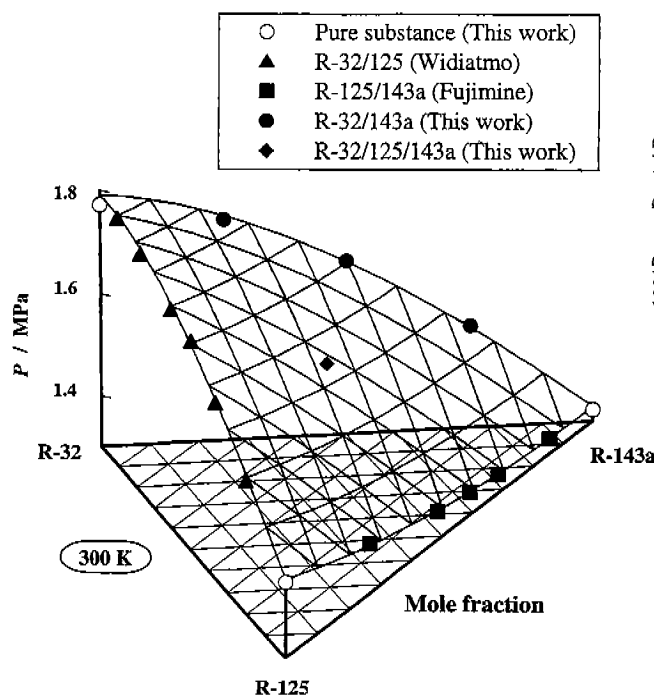


Fig. 2 Bubble-point pressure at 300 K

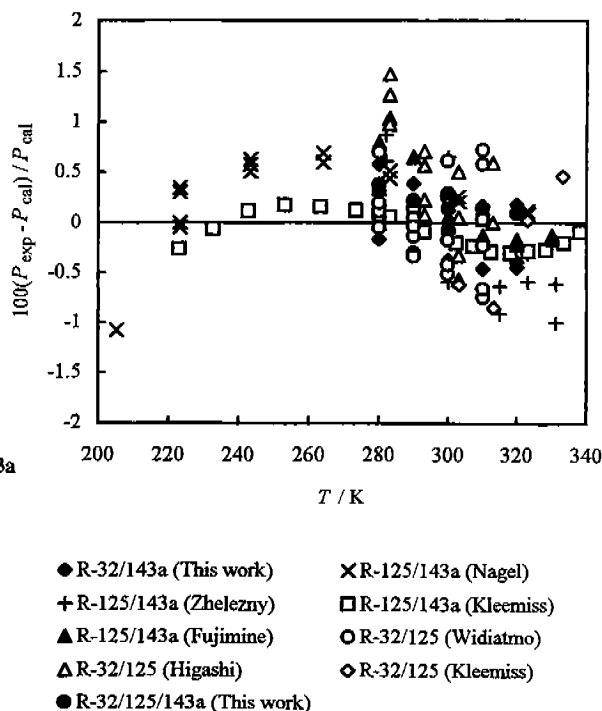


Fig. 3 Pressure deviation from the PR eq.

The bubble-point pressure deviation from the PR equation is depicted in Fig. 3. Also shown in Fig. 3 are the available bubble-point pressures reported by Kleemiss [7], Nagel et al. [8], Zhelezny et al. [9] and by Higashi et al. [10]. Except some data by Higashi et al. which show a strong temperature dependence and a single datum by Nagel et al., the optimized PR equation, as observed from Fig. 3, represents the available measured data well within $\pm 1\%$. Figure 3 also illustrates the deviation of the measured bubble-point pressures of the ternary R-32/125/143a system from the PR equation, which has been developed only by introducing the binary interaction parameter given in Table 2 for the binary R-32/125, R-32/143a and R-125/143a systems. The composition of the ternary R-32/125/143a system where the bubble-point pressures are to be measured was chosen being 33.56/33.28/33.16 mol% on the basis of a consideration that it would be the most probable location for any change in the bubble-point pressure surface. Figure 3 indicates that the PR equation optimized with the proposed procedure represents satisfactorily the bubble-point pressures of the ternary R-32/125/143a system. The difference between the measured and calculated bubble-point pressures is within ± 5 kPa.

The measured saturated-liquid densities of the present mixtures at 300 K are illustrated in Fig. 4 where the isopleth lines are calculated from the developed saturated-liquid density correlation given in Eq. (1). This type of equation has also been successfully applied to the binary refrigerant mixtures composed of R-32, R-125 and R-134a [11].

$$\frac{\rho_s}{\rho_{cm}} - 1 = A_m \left(1 - \frac{T}{T_{cm}} \right)^{a_m} + B_m \left(1 - \frac{T}{T_{cm}} \right)^{b_m} + C_m \left(1 - \frac{T}{T_{cm}} \right)^{c_m} \quad (1)$$

where ρ_s denotes the saturated-liquid density, ρ_{cm} and T_{cm} the pseudo-critical density and temperature, respectively, and the subscript m the mixture.

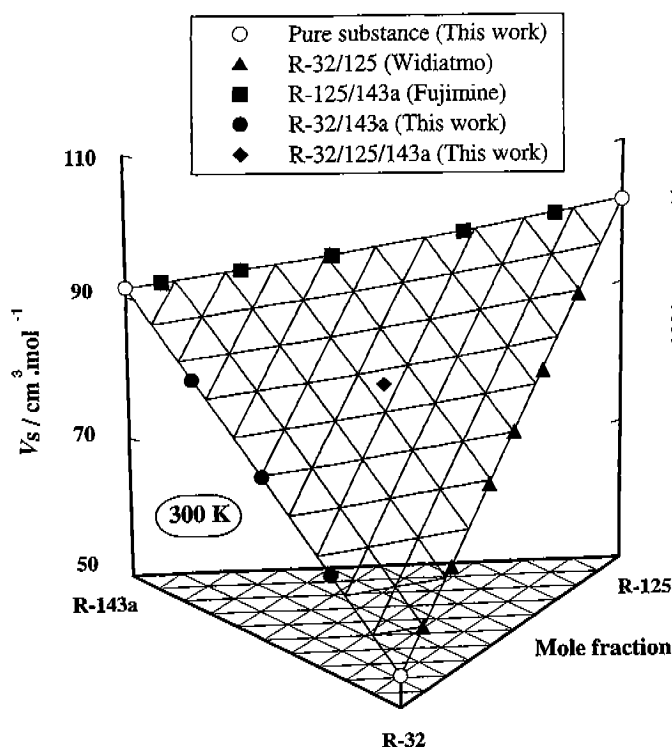


Fig. 4 Saturated-liquid molar volumes at 300 K

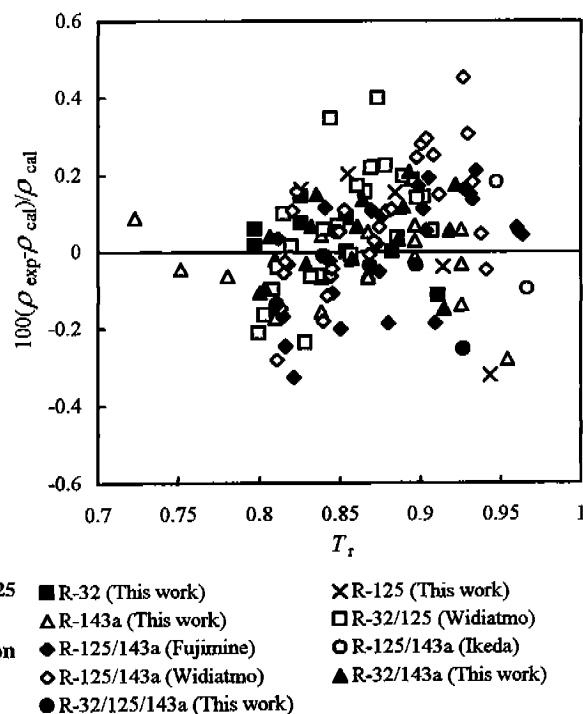


Fig. 5 Density deviation from Eq. (1)

The pseudo-critical temperatures and critical densities for the mixture, and coefficients a_m , b_m , A_m , and B_m are simply correlated by Eq. (2) where M represents an arbitrary parameter of the present interest. The critical temperature and critical density values for pure refrigerants are listed in Table 1, while the numerical constants a_m , b_m , c_m , A_m , B_m , and C_m are given in Table 3.

$$M_m = M_1 x_1 + M_2 x_2 + M_3 x_3 \quad (2)$$

Equation (2) is used by replacing M with the desired mixing parameter in Eq. (1). Subscripts 1, 2 and 3 in Eq. (2) represents R-32, R-125 and R-143a, respectively. Figure 5 denotes the deviation of measured saturated-liquid densities from Eq. (1). Also shown in Fig. 5 are our saturated-liquid density data of the binary R-32/125 and R-125/143a systems

reported elsewhere [1, 2] and the data by Ikeda et al. [12]. Figure 5 shows that Eq. (1) represents satisfactorily most of the saturated-liquid densities of the binary and ternary mixtures of the present interest within $\pm 0.4\%$.

Table 3 Numerical Constants used in Eq. (2)

	R-32	R-125	R-143a
A_i	0.88472	0.69199	0.86085
B_i	2.0797	1.4714	1.7132
C_i	0	0.49887	0.13684
a_i	0.194	0.770	0.551
b_i	0.629	0.454	0.434
c_i	0	0.156	0.001

Measured compressed-liquid densities of the refrigerant mixtures in the present study are well represented by Eq. (3), which is a modification of the equation of state for water developed by Sato [13].

$$\rho/\rho_{cm} = (P/P_{cm} + D)^E/C \quad (3)$$

where

$$C = c_1\tau + c_2\tau^2 + c_3\tau^4 + c_4\tau^6 + c_5\tau^9 \quad (4)$$

$$D = d_1\tau + d_2\tau^2 + d_3\tau^3 + d_4\tau^6 \quad (5)$$

$$E = e_1 + e_2\tau \quad (6)$$

and

$$\tau = 1 - T/T_{cm} \quad (7)$$

The pseudo-critical temperature, critical pressure and critical density of mixtures are obtained by using Eq. (2), whereas the coefficients in Eqs. (4) through (6) are calculated from Eq. (8) with numerical constants given in Table 4. Equation (8) is used by replacing L with c_i , d_i , or e_i in Eqs. (4) through (6). The effectiveness of Eq. (3) has been confirmed in the present study to reproduce the measured density data at temperatures from 280 to 320 K and pressures up to 3 MPa within $\pm 0.4\%$.

$$L_i = l_{i1}x_1 + l_{i2}x_2 + l_{i3}x_3 + l_{i12}x_1x_2 + l_{i13}x_1x_3 + l_{i23}x_2x_3 \quad (8)$$

Table 4 Numerical Constants in Eq. (8)

	l_{i1}	l_{i2}	l_{i3}	l_{i12}	l_{i23}	l_{i31}
c_1	9.3250	20.446	15.460	2.6588	-1.0321	1.8830
c_2	88.168	145.09	90.049	-1.5382	-0.064931	0.85802
c_3	1580.7	-63.955	897.99	-0.025569	0.053405	0.15620
c_4	3082	-14685	-5008.9	0.0013138	0.0028698	0.011527
c_5	0.38295	3.6986	-2.3159	-0.00029069	0.00015945	0.00038277
d_1	-1892.6	-9097.0	-3677.7	0	0	0
d_2	-51.670	-64.482	-49.777	0	0	0
d_3	1418.6	3048.7	1893.4	0	0	0
d_4	39.473	40.060	50.957	0	0	0
e_1	0.52049	0.57874	0.56456	0	0	0
e_2	1.7047	1.2830	1.2165	0	0	0

On the basis of our analysis in optimizing the PR equation, it is possible to calculate the temperature glides generated by the refrigerant mixtures of R-32, R-125 and R-143a. Temperature glide, a difference between the bubble-point and dew-point temperature, $T_d - T_b$, is one of the important measures for selecting the optimum refrigerant suitable to the vapor-compression cycle. Figure 6 illustrates the temperature glides for different refrigerant mixtures at 500 kPa. The mixtures consisted of R-32, R-125 and/or R-143a have relatively small temperature glides within 1 K. With such small temperature glides the refrigerant mixtures would behave more or less similarly as a pure refrigerant.

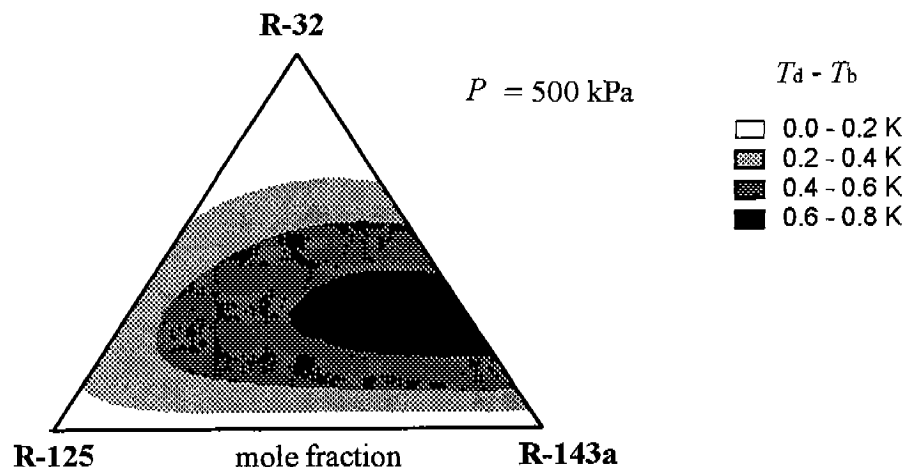


Fig. 6 Temperature glides for different refrigerant mixtures

CONCLUSION

The bubble-point pressures and the liquid densities of the refrigerant mixtures constituted by R-32, R-125 and/or R-143a have been studied experimentally. The temperature glides derived from the Peng-Robinson equation optimized in the present study, by which a data representation within $\pm 1\%$ has been obtained, was within 1 K. The measured liquid densities were also well represented by the correlations developed in the present work.

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